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MEASUREMENT AND INTERPRETATION OF ACIDITY IN SOUTHERN CALIFORNIA RAINFALL AND AEROSOLS

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Measurement and Interpretation of Acidity in Southern California Rainfall and Aerosols

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The semiarid climate of southern California and relatively high air pollutant concentrations during the dry season lead to a higher dry flux than wet flux of acidity. Additional research is needed to measure the dry flux as well as ambient ammonia concentrations. The relative importances of the dry flux, wet flux and advection for the Los Angeles Basin are summaried in Table 8.1. The wet flux is about an order of magnitude less than the total dry flux, although it is greater than the dry flux due to aerosol deposition. Of the acids and bases released in the basin, more than half are exported out of the basin by advection.

Modeling the wet flux is of interest because of unique environmetal conditions in the Los Angeles Basin:

1. Wind trajectories show that southern California is not immediately downwind of any major pollutant sources. The wet deposition is due to local sources rather than long range transport.

2. Equivalent emissions of NO_x are more than twice the equivalent emissions of SO_x in the Los Angeles air shed. Consequently, nitric to sulfuric acid equivalent ratios in precipitation are higher than those reported in the northeastern United States and in northern Europe.

3. The high photochemical activity in the Los Angeles air shed catalyzes the precipitation scavenging of nitrates relative to sulfates. The nitric acid contribution was greater in Pasadena from February

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TABLE 8.1

ACID AND BASE BALANCE FOR THE LOS ANGELES BASIN

	Emissions[1]	Measured Wet Flux[2]	Calculated Dry Flux[3]	Advection and Chemical Oxidation/Reduction of Acids/Bases to Neutral Species
$SO_2 - SO_4^{2-}$	9400	210	2400	6790
$NO - NO_2 - NO_2^- - NO_3^-$	22000	160	5600	16240
$NH_3 - NH_4^+$		130	<1450[5]	

1. Based on 1975-1976 data.

2. Based on 1978-1979 data.

3. Based on 1976-1977 data.

4. Calculated by difference (emissions - wet - dry = advection).

5. Based on assumed p_{NH_3}.

All values given in units equivalents/HA-YR.

1976 to November 1977 than from December 1977 to April 1979, the earlier period being characterized by light precipitation and high photochemical activity before each storm and the latter period by heavy winter storms.

The wet flux of acidity has been characterized several ways:

1. Monitoring has described the temporal distributions of acidity. Temporal variations of precipitation concentrations by hour of day, day of week and month of year reflect precipitation characteristics (precipitation intensity, strength of frontal system or amount of advection, precipitation type, etc.) rather than temporal variations of emissions.

2. Spatial distributions of acidity reflect spatial distributions of acids and bases and precipitation amount. In general, ammonium concentrations increase from the coast to inland areas, non-sea salt sulfate decreases from the coastal to inland sites, and nitrate to sulfate ratios increase from coastal to eastern basin and mountain sites. Higher precipitation in the mountains results in lower concentrations than at basin sites, but the acid fluxes are comparable between the mountain and eastern basin sites.

3. Surface and upper air wind trajectory models for Pasadena reflect precipitation characteristics rather than spatial variations of sources.

4. A source strength model has used chemical tracers to identify the contributions of natural and anthropogenic sources to rainwater quality. The major sources are sea salt, soil dust and ammonia alkalinity plus sulfate (primarily due to stationary sources) and nitrate (primarily due to mobile sources) acidity. To confirm the contributions of stationary and mobile sources to rainwater sulfates and nitrates, stable isotope ratios of precipitation sulfur and nitrogen should be characterized and used as tracers.

5. The mean and extreme values of rainwater quality are described by the log-normal distribution.

Models used in this study to predict rainwater quality were only semi-quantitative:

1. Linear regression models of nitrite plus nitrate and sulfate concentrations based on ground level air quality measurements accounted for less than 60 percent of the variance in rainwater concentrations. Nitrite plus nitrate and sulfate concentrations in rainwater showed dependence on NO, O_3, and aerosol Pb concentrations measured at ground level as well as precipitation intensity. Other independent variables showed variance ratios significant at the 95 percent confidence level for Pasadena samples including temperature and relative humidity.

2. Equilibrium models failed to predict rainwater sulfate and nitrate concentrations. Equilibrium models were useful in predicting nitrite concentrations (less than 1 μM) and the partial pressure of ammonia during precipitation (approximately 0.003 ppb). Equilibrium models also estimated the total sulfite contribution to total sulfur in precipitation (10-25 percent) and provided a clay dissolution relationship between aluminum and silicate concentrations.

3. Aqueous kinetic models of nitrate and sulfate concentrations underestimated measured values. Research into the Kinetics of oxidation processes during gas scavenging is needed to determine the mechanisms of nitrate and sulfate formation in rainwater.

4. Models of concentration changes during a storm worker for some species in individual storms but offered no general predictive capability.

The concept of atmospheric acidity was developed to allow acidity balances and to emphasize the acid-base character of gaseous and aerosol species. Atmospheric acidity encompasses strong acid plus base systems, strong and weak acid plus base systems, acid/base systems involved in oxidation-reduction reactions as well as acid-base specialtion in the gas, aerosol and precipitation phases. The importance of redox

reactions in changing acid-base speciation should be quantified to model the impact of acid fluxes in the terrestrial environment. The average dry fluxes calculated by this investigation should be refined with emphasis on the probability of extreme values which are needed to model biological impacts.

This project element will be continued and possibly expanded in the coming year. The monitoring network will be maintained and the data gathered will be used to build on the established base. Changes in acidity in rainfall and aerosols due to variations in the character of emissions in the Los Angeles basin will be especially looked for.

In addition, preliminary work will be started in analyzing trace organic compounds found in rainfall and in relating them to trace organics found in the atmosphere.

PUBLICATIONS FROM PROJECT ELEMENT NO. 8

8a. H. M. Liljestrand and J. J. Morgan, "Chemical Composition of Acid Precipitation in Pasadena, California," Environmental Science and Technology, vol. 12, pp. 1271-73, 1978.

8b. H. M. Liljestrand, "Atmospheric Transport of Acidity in Southern California by Wet and Dry Mechanisms," Ph.D. thesis, Division of Engineering and Applied Science, California Institute of Technology, Pasadena, California, August 27, 1979.

8c. H. M. Liljestrand and J. J. Morgan, "Error Analysis Applied to Indirect Methods for Precipitation Acidity," Tellus (to be published), 1979.